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FINAL REPORT

SYNTHESIS AND CHARACTERIZATION OF NEW LOW-DIMENSIONAL
TRANSITION METAL COMPLEX CONDUCTORS

BY
WILLIAM E. HATFIELD
UNIVERSITY OF NORTH CAROLINA
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FINAL REPORT

1. **Summary:** This research program was devoted to the designed synthesis and characterization of new transition metal complex conductors. Also, in keeping with good scientific practice, unusual fundamental observations discovered during the course of the research were given attention as discussed in End of the Year Reports, Technical Reports, and orally. The design of the new compounds was based on sound scientific principles developed in our laboratory and in other laboratories around the world. The new compounds were characterized by temperature-dependent AC and DC electrical conductivity measurements, magnetic susceptibility and electron paramagnetic resonance, structural determinations by single-crystal X-ray diffraction, and by other spectroscopic techniques, as appropriate. The results of the research contributed significantly to practical and fundamental knowledge, provided educational opportunities for a number of undergraduate students, graduate students, and research associates. The work attracted attention of the scientific and technical community and stimulated activities in laboratories around the world (see the list of authors in the publications cited below). Brief reviews of important results are present in the following paragraphs.

Bis-Macrocyclic-Lanthanide Compounds: Many of the compounds studied were mixed-valence or non-stoichiometric and exhibited high and anisotropic electrical conductivities. Remarkable fundamental results include the discovery of strong exchange coupling between the lanthanide ions and the ligand radicals. Previously, it was contended that f-electrons are highly shielded and are essentially unaffected by the nature of the ligands. This entire line of reasoning will have to be re-examined. Also, it was found that some of these compounds have large magnetic moments, even though they did not have unpaired electrons. These are the first compounds found to exhibit such properties. (See technical report no. 45).

Since these compounds are electrochromic, there has been much technical and fundamental work aimed toward their use in devices. Through other support we have made polymeric thin-film layers on appropriate substrates and have made sandwiches on the polymers. The work is in preliminary stages and will form the basis for an honors research project in the coming year.

New Materials with High Dielectric Properties: Polymeric materials most frequently have low dielectric constants, and blends are usually compounded to enhance dielectric properties. There are significant problems with these substances, and we have launched a program designed to produce processable polymers with high dielectric constants. This program was described in the 1993 End of the Year Report, where scientific details may be found. The program has attracted the attention of industrial concerns who have the capability of commercializing useful materials that will be produced.

2. Technical Reports Resulting from the Grant:

No. 45. Trojan, K. L.; Kendall, J. L.; Kepler, K. D.; Hatfield, W. E. "Strong Exchange Coupling Between the Lanthanide Ions and the Phthalocyaninato Ligand Radical in Bis(phthalocyaninato)lanthanide Sandwich Compounds", July 6, 1992.

No. 46. Kim, Y. I.; Hatfield, W. E. "Electrical, Magnetic, and Spectroscopic Properties of $(TTF)_5Fe(NO_3)_3$ ", December 15, 1992.

3. Journal Articles Acknowledging That the Research Was Partially Supported by the Office of Naval Research:

Trojan, K. L.; Kendall, J. L.; Kepler, K. D.; Hatfield, W. E. "Strong Exchange Coupling Between the Lanthanide Ions and the Phthalocyaninato Ligand Radical in Bis(phthalocyaninato)-lanthanide Sandwich Compounds" Inorg. Chim. Acta, 1992, 200, 795-803.

Oki, A. R.; Zhang, H.; Maguire, J. A.; Hosmane, N. S.; Ro, H.-K.; Hatfield, W. E.; Moscherosch, M.; Kaim, W. "Chemistry of C-Trimethylsilyl-Substituted Heterocarboranes. 10. Syntheses, Structures and Properties of Anionic Cr(III) and Neutral Cr(IV) Sandwiched Metallacarborane Complexes $(1,1'\text{-}\underline{\text{commo}}\text{-Cr}[2\text{-(SiMe}_3\text{)}_3\text{-3-(R)-2,3-C}_2\text{B}_4\text{H}_4\text{]}_2)^-$ and $1,1'\text{-}\underline{\text{commo}}\text{-Cr}[2,3\text{-(SiMe}_3\text{)}_2\text{-2,3-C}_2\text{B}_4\text{H}_4\text{]}_2$ (R = SiMe₃, Me and H)" Organometallics, 1992, 11, 4202-4213.

Kim, Y. I.; Hatfield, W. E. "Electrical, Magnetic, and Spectroscopic Properties of $(TTF)_5Fe(NO_3)_3$ ", Inorg. Chim. Acta, 1992, 204, 261-263.

Hatfield, W. E.; Trojan, K. L.; White, P. S.; Horner, O.; ter Haar, L. W.; Nelson, D. J.; Cervantes-Lee, F.; Hoffmann, S. K.; Hilczer, W.; Gosler, J.; Hitchman, M. A. Mol. Cryst. Liq. Cryst., 1993, 233, 309-316.

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